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<b>(21) International Application Number:</b> PCT/GB99/02121 <b>(22) International Filing Date:</b> 2 July 1999 (02.07.99) <b>(30) Priority Data:</b> 9816077.3 24 July 1998 (24.07.98) GB <b>(71) Applicant (for all designated States except US):</b> THE SECRETARY OF STATE FOR DEFENCE [GB/GB]; Defence Evaluation and Research Agency, Ively Road, Farnborough, Hampshire GU14 0LX (GB). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> BADYAL, Jas, Pal, Singh [GB/GB]; University of Durham, Science Laboratories, South Road, Durham DH1 3LE (GB). COULSON, Stephen, Richard [GB/GB]; University of Durham, Science Laboratories, South Road, Durham DH1 3LE (GB). WILLIS, Colin, Robert [GB/GB]; CBDE, Porton Down, Salisbury, Wiltshire SP4 0JQ (GB). BREWER, Stuart, Anson [GB/GB]; CBDE, Porton Down, Salisbury, Wiltshire SP4 0JQ (GB). <b>(74) Agent:</b> BOWDERY, A., O.; D/IPR, Formalities Section, Poplar 2, MOD Abbey Wood # 19, Bristol BS34 8JH (GB).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> SURFACE COATINGS  <b>(57) Abstract</b>  A method of coating a surface with a polymer layer, which method comprises exposing said surface to a pulsed plasma comprising a monomeric saturated organic compound, said compound comprising an optionally substituted alkyl chain of at least 5 carbon atoms optionally interposed with a heteroatom, such as a halo substituted alkane; so as to form an oil or water repellent coating on said substrate. Substrates such as fabrics obtained by this process are also claimed.		

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Surface Coatings

The present invention relates to the coating of surfaces, in particular to the production of oil- and water- repellent surfaces, as well as to coated articles obtained thereby.

Oil- and water- repellent treatments for a wide variety of surfaces are in widespread use. For example, it may be desirable to impart such properties to solid surfaces, such as metal, glass, ceramics, paper, polymers etc. in order to improve preservation properties, or to prevent or inhibit soiling.

A particular substrate which requires such coatings are fabrics, in particular for outdoor clothing applications, sportswear, leisurewear and in military applications. Their treatments generally require the incorporation of a fluoropolymer into or more particularly, fixed onto the surface of the clothing fabric. The degree of oil and water repellency is a function of the number and length of fluorocarbon groups or moieties that can be fitted into the available space. The greater the concentration of such moieties, the greater the repellency of the finish.

In addition however, the polymeric compounds must be able to form durable bonds with the substrate. Oil- and water- repellent textile treatments are generally based on fluoropolymers that are applied to fabric in the form of an aqueous emulsion. The fabric remains breathable and permeable to air since the treatment simply coats the fibres with a very thin, liquid-repellent film. In order to make these finishes durable, they are sometimes co-applied with cross-linking resins that bind the fluoropolymer to fibres. Whilst good levels of durability towards laundering and dry-

cleaning can be achieved in this way, the cross-linking resins can seriously damage cellulosic fibres and reduce the mechanical strength of the material. Chemical methods for producing oil- and water-repellent textiles are disclosed  
5 for example in WO 97/13024 and British patent No 1,102,903 or M. Lewin et al., 'Handbook of Fibre Science and Technology' Marcel and Dekker Inc., New York, (1984) Vol 2, Part B Chapter 2.

10 Plasma deposition techniques have been quite widely used for the deposition of polymeric coatings onto a range of surfaces. This technique is recognised as being a clean, dry technique that generates little waste compared to conventional wet chemical methods. Using this method,  
15 plasmas are generated from small organic molecules, which are subjected to an ionising electrical field under low pressure conditions. When this is done in the presence of a substrate, the ions, radicals and excited molecules of the compound in the plasma polymerise in the gas phase and react  
20 with a growing polymer film on the substrate. Conventional polymer synthesis tends to produce structures containing repeat units which bear a strong resemblance to the monomer species, whereas a polymer network generated using a plasma can be extremely complex.

25 The success or otherwise of plasma polymerisation depends upon a number of factors, including the nature of the organic compound. Reactive oxygen containing compounds such as maleic anhydride, has previously been subjected to plasma  
30 polymerisation (Chem. Mater. Vol. 8, 1, 1996).

US Patent No 5,328,576 describes the treatment of fabric or paper surfaces to impart liquid repellent properties by

subjecting the surfaces to a pre-treatment with an oxygen plasma, followed by plasma polymerisation of methane.

However, plasma polymerisation of the desirable oil and  
5 water repellent fluorocarbons have proved more difficult to achieve. It has been reported that cyclic fluorocarbons undergo plasma polymerisation more readily than their acyclic counterparts (H. Yasuda et al., J. Polym. Sci., Polym. Chem. Ed. 1977, 15, 2411). The plasma polymerization  
10 of trifluoromethyl-substituted perfluorocyclohexane monomers has been reported (A. M. Hynes et al., Macromolecules, 1996, 29, 18-21).

A process in which textiles are subjected to plasma  
15 discharge in the presence of an inert gas and subsequently exposed to an F-containing acrylic monomer is described in SU-1158-634. A similar process for the deposition of a fluoroalkyl acrylate resists on a solid substrate is described in European Patent Application No. 0049884.

20 Japanese application no. 02011606 describes the plasma polymerisation of compounds including fluorosubstituted acrylates. In that process, a mixture of the fluorosubstituted acrylate compounds and an inert gas are  
25 subjected to a glow discharge.

Copending International Patent application based upon British Patent Application Nos. 9712338.4 and 9720078.6 describes a method method for producing polymer and  
30 particular halopolymer coatings which are water and/or oil repellent on surfaces by the plasma deposition of monomer compounds which include carbon-carbon double bonds. The applicants have found that the method can be extended to the deposition of other compounds. In particular monomers which

are unsaturated in that they contain no carbon-carbon double bonds may be employed in the process and similar advantageous results achieved.

- 5 According to the present invention there is provided a method of coating a surface with a polymer layer, which method comprises exposing said surface to a pulsed plasma comprising a monomeric saturated organic compound, said compound comprising an optionally substituted alkyl chain of  
10 at least 5 carbon atoms optionally interposed with a heteroatom; so as to form an oil or water repellent coating on said substrate.

The term "saturated" as used herein means that the monomer  
15 does not contain multiple bonds (i.e. double or triple bonds) between two carbon atoms which are not part of an aromatic ring. The term "heteroatom" includes oxygen, sulphur, silicon or nitrogen atoms. Where the alkyl chain is interposed by a nitrogen atom, it will be substituted so  
20 as to form a secondary or tertiary amine. Similarly, silicons will be substituted appropriately, for example with two alkoxy groups.

Other terms used herein include "halo" or "halogen" which  
25 refer to fluorine, chlorine, bromine and iodine. Particularly preferred halo groups are fluoro. The term "aryl" refers to aromatic cyclic groups such as phenyl or naphthyl, in particular phenyl. The term "alkyl" refers to straight or branched chains of carbon atoms, suitably of up  
30 to 50 carbon atoms in length. Derivatives of alkyl groups, such as would be understood by "alkoxy" include such groups. The term "heterocyclyl" includes aromatic and non aromatic rings or ring systems, suitably containing up to 12 atoms, up to three of which may be heteroatoms.

The monomeric compound used in the process of the invention may comprise one or more optionally substituted alkyl chains, either as part of a branched alkane or as part of a more complex structure including rings and other functional groups. These may be present either in the monomer used as a starting material, or may be created in the monomer on application of the plasma, for example by the ring opening of an optionally substituted cycloalkyl monomer.

10

Suitable optional substituents for the monomeric compounds of the invention include halo, cyano, nitro, oxo, epoxide, optionally substituted cycloalkyl, optionally substituted aryl, optionally substituted aralkyl, optionally substituted heterocyclyl,  $C(O)_nR^1$ ,  $OR^1$ ,  $S(O)_mR^1$ ,  $NR^2R^3$ ,  $C(O)NR^2R^3$ ,  $OC(O)NR^2R^3$ ,  $=NOR^2$ ,  $-NR^2C(O)_nR^2$ ,  $-NR^1CONR^2R^3$ ,  $-C=NOR^1$ ,  $-N=CR^2R^3$ ,  $S(O)_mNR^2R^3$  or  $-NR^2S(O)_mR^1$  where  $R^1$ ,  $R^2$  and  $R^3$  are independently selected from hydrogen or alkyl, aralkyl, cycloalkyl, aryl or heterocyclyl, any of which may be optionally substituted, or  $R^2$  and  $R^3$  together form an optionally substituted ring which optionally contains further heteroatoms such as sulphur, oxygen and nitrogen,  $n$  is an integer of 1 or 2,  $m$  is 0 or an integer of 1-3.

Suitable optional substituents for aryl, aralkyl and cycloalkyl and heterocyclyl groups  $R^1$ ,  $R^2$  and  $R^3$  include halo, perhaloalkyl, mercapto, hydroxy, alkoxy, oxo, heteroaryloxy, alkenyloxy, alkynyloxy, alkoxyalkoxy, aryloxy (where the aryl group may be substituted by halo, nitro, or hydroxy), cyano, nitro, amino, mono- or di-alkyl amino, alkylamido or oximino.

Suitable alkyl chains, which may be straight or branched, have from 5 to 50 carbon atoms, more suitably from 6 to 20

carbon atoms, and preferably from 8 to 15 carbon atoms, provided at least 5 carbon atoms form a straight chain.

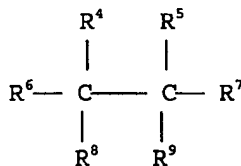
- 5 Monomeric compounds where the chains comprise unsubstituted alkyl groups are suitable for producing coatings which are water repellent. By substituting at least some of the hydrogen atoms in these chains with at least some halogen atoms, oil repellency may also be conferred by the coating.

10

Thus in a preferred aspect, the monomeric compounds include haloalkyl moieties or comprise haloalkyls. Therefore, preferably the plasma used in the method of the invention will comprise a monomeric saturated haloalkyl containing  
15 organic compound.

Particularly suitable monomeric organic compounds are those of formula (I)

20



25

- where  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$  and  $\text{R}^8$  are independently selected from hydrogen, halogen, alkyl, haloalkyl or aryl optionally substituted by halo; and  $\text{R}^9$  is a group  $\text{X}-\text{R}^{10}$  where  $\text{R}^{10}$  is an  
30 alkyl or haloalkyl group and X is a bond; a group of formula  $-\text{C}(\text{O})\text{O}(\text{CH}_2)_x\text{Y}-$  where x is an integer of from 1 to 10 and Y is a bond or a sulphonamide group; or a group -  
(O)<sub>p</sub> $\text{R}^{11}$ (O)<sub>s</sub>(CH<sub>2</sub>)<sub>t</sub>- where  $\text{R}^{11}$  is aryl optionally substituted by halo, p is 0 or 1, s is 0 or 1 and t is 0 or an integer of  
35 from 1 to 10, provided that where s is 1, t is other than 0.



7

Suitable haloalkyl groups for  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^6$ , and  $R^8$  are fluoroalkyl groups. The alkyl chains may be straight or branched and may include cyclic moieties and have, for example from 1 to 6 carbon atoms.

5

For  $R^{10}$ , the alkyl chains suitably comprise 1 or more carbon atoms, suitably from 1-20 carbon atoms and preferably from 6 to 12 carbon atoms.

- 10 Preferably  $R^{10}$  is a haloalkyl, and more preferably a perhaloalkyl group, particularly a perfluoroalkyl group of formula  $C_zF_{2z+1}$ , where  $z$  is an integer of 1 or more, suitably from 1-20, and preferably from 6-12 such as 8 or 10.
- 15 Where  $X$  is a group  $-C(O)O(CH_2)_yY-$ ,  $y$  is an integer which provides a suitable spacer group. In particular,  $y$  is from 1 to 5, preferably about 2.

- Suitable sulphonamide groups for  $Y$  include those of formula
- 20  $-N(R^{11})SO_2^-$  where  $R^{11}$  is hydrogen, alkyl or haloalkyl such as  $C_{1-4}$ alkyl, in particular methyl or ethyl.

- The monomeric compounds used in the method of the invention preferably comprises an  $C_{6-25}$ alkane optionally substituted by
- 25 halogen, in particular a perhaloalkane, and especially a perfluoroalkane.

- Compounds of formula (I) are either known compounds or they can be prepared from known compounds using conventional
- 30 methods.

Suitable plasmas for use in the method of the invention include non-equilibrium plasmas such as those generated by alternating current (AC) (e.g. radiofrequencies (Rf),

microwaves) or direct current (DC). They may operate at atmospheric or sub-atmospheric pressures as are known in the art.

- 5 The plasma may comprise the monomeric compound alone, in the absence of other gases or in mixture with for example an inert gas. Plasmas consisting of monomeric compound alone may be achieved as illustrated hereinafter, by first  
10 evacuating the reactor vessel as far as possible, and then purging the reactor vessel with the organic compound for a period sufficient to ensure that the vessel is substantially free of other gases.

The surface coated in accordance with the invention may be  
15 of any solid substrate, such as fabric, metal, glass, ceramics, paper or polymers. In particular, the surface comprises a fabric substrate such as a cellulosic fabric, to which oil- and/or water-repellency is to be applied. Alternatively, the fabric may be a synthetic fabric such as  
20 an acrylic/nylon fabric.

The fabric may be untreated or it may have been subjected to earlier treatments. For example, it has been found that treatment in accordance with the invention can enhance the  
25 water repellency and confer a good oil-repellent finish onto fabric which already has a silicone finish which is water repellent only.

Precise conditions under which the plasma polymerization  
30 takes place in an effective manner will vary depending upon factors such as the nature of the polymer, the substrate etc. and will be determined using routine methods and/or the techniques illustrated hereinafter. In general however, polymerisation is suitably effected using vapours of

compounds of formula (I) at pressures of from 0.01 to 10 mbar, suitably at about 0.2mbar.

A glow discharge is then ignited by applying a high  
5 frequency voltage, for example at 13.56MHz.

The applied fields are suitably of average power of up to 50W. Suitable pulsed fields are those which are applied in a sequence which yields very low average powers, for example  
10 of less than 10W and preferably of less than 1W. Examples of such sequences are those in which the power is on for 20 $\mu$ s and off for from 10000 $\mu$ s to 20000 $\mu$ s.

The fields are suitably applied for a period sufficient to  
15 give the desired coating. In general, this will be from 30 seconds to 3 hours, preferably from 2 to 30 minutes, depending upon the nature of the monomer compound used and the substrate etc.

20 Plasma polymerisation in accordance with the invention particularly at low average powers has been found to result in the deposition of highly fluorinated coatings which exhibit super-hydrophobicity.

25 In a preferred embodiment, the pulses are applied at a variable rate, with relatively long pulses applied, for example of from 1 to 10 secs on initially, reducing down to short pulses for example of from 100 $\mu$ s to 1 $\mu$ s on and 10 $\mu$ s to 1000 $\mu$ s off, later in the process. It is believed that such  
30 a regime leads to improved coatings because the initial long pulse leads to greater fragmentation of the monomer, leading to a more disorganised and therefore strongly bonding layer directly adjacent the substrate. Shorter late pulses means that the upper layers deposited retain a more organised

structure and so contain a greater number of long chains, which are responsible for the oil and water repellency on the surface.

- 5 Suitably the compound of formula (I) includes a perfluoroalkylated tail or moiety, in which case, the coating obtained by the process of the invention may have oleophobic as well as hydrophobic surface properties.
- 10 Thus the invention further provides a hydrophobic or oleophobic substrate which comprises a substrate comprising a coating of a alkyl polymer and particularly a haloalkyl polymer which has been applied by the method described above. In particular, the substrates are fabrics but they
- 15 may be solid materials such as biomedical devices.

In a further aspect the invention provides the use of an optionally substituted alkane or optionally substituted cycloalkane having at least 5 carbon atoms and particularly

20 a perhaloalkane in the production of water and/or oil repellent coatings by pulsed plasma deposition methods.

The invention will now be particularly described by way of example with reference to the accompanying diagrammatic

25 drawings in which:

Figure 1 shows a diagram of the apparatus used to effect plasma deposition; and

- 30 Figure 2 is a graph showing the characteristics of pulsed wave plasma polymerisation of perfluorododecane.

Example 1Plasma Polymerisation of perfluorododecane

Perfluorododecane ( $C_{12}F_{26}$ ) was placed into a monomer tube (1) (Fig. 1). A series of plasma polymerisation experiments were carried out in an inductively coupled cylindrical plasma reactor vessel (2) of 5cm diameter, 470cm<sup>3</sup> volume, base pressure of  $7 \times 10^{-3}$  mbar, and with a leak rate of better than  $2 \times 10^{-3}$  cm<sup>3</sup>min<sup>-1</sup>. The reactor vessel (2) was connected by way of a "viton" O-ring (3), a gas inlet (4) and a needle valve (5) to the monomer tube (1).

A thermocouple pressure gauge (6) was connected by way of a Young's tap (7) to the reactor vessel (2). A further Young's tap (8) connected with an air supply and a third (9) lead to an E2M2 two stage Edwards rotary pump (not shown) by way of a liquid nitrogen cold trap (10). All connections were grease free.

An L-C matching unit (11) and a power meter (12) was used to couple the output of a 13.56 Mhz R.F. generator (13), which was connected to a power supply (14), to copper coils (15) surrounding the reactor vessel (2). This arrangement ensured that the standing wave ratio (SWR) of the transmitted power to partially ionised gas in the reactor was as low as possible. A pulse generator (16) was used to trigger the R.F.

power supply, and a cathode ray oscilloscope (17) was used to monitor the pulse width and amplitude. The average power  $\langle P \rangle$  delivered to the system during pulsing is given by the following formula:

$$\langle P \rangle = P_{cw} \{ T_{on} / (T_{on} + T_{off}) \}$$

where  $T_{on}/(T_{on} + T_{off})$  is defined as the duty cycle and  $P_{cw}$  is the average continuous wave power.

In order to carry out polymerization/deposition reactions  
5 the reactor vessel (2) was cleaned by soaking overnight in a  
chloros bleach bath, then scrubbing with detergent and  
finally rinsing with isopropyl alcohol followed by oven  
drying. The reactor vessel (2) was then incorporated into  
the assembly as shown in Figure 1 and further cleaned with a  
10 50W air plasma for 30 minutes. Next the reactor (2) vessel  
was vented to air and the substrate to be coated (19), in  
this case a glass slide, was placed in the centre of the  
chamber defined by the reactor vessel (2) on a glass plate  
(18). The chamber was then evacuated back down to base  
15 pressure ( $7.0 \times 10^{-3}$  mbar).

Perfluoroalkane vapour was then introduced into the reaction  
chamber at a constant pressure of ~0.2mbar and allowed to  
purge the plasma reactor, followed by ignition of the glow  
20 discharge. Typically 2-15 minutes deposition time was found  
to be sufficient to give complete coverage of the substrate.  
After this, the R.F generator was switched off and the  
perfluoroalkane vapour allowed to continue to pass over the  
substrate for a further 5 minutes before evacuating the  
25 reactor back down to base pressure, and finally venting up  
to atmospheric pressure.

The experiments were carried out with average powers in the  
range of from 0.3 to 50W. The XPS spectrum of the product  
30 of a pulsed wave plasma polymer deposition onto a glass  
slide was taken.

Figure 2 shows the C (1s) XPS spectrum for a 5 minute pulsed plasma polymerisation experiment where:-  $P_{cw} = 70W$

$$T_{on} = 20\mu s$$

5  $T_{off} = 20000\mu s$   $\langle P \rangle = 0.07W$

The chemical composition of the deposited coating for pulsed plasma deposition is given in Table 2 below.

10

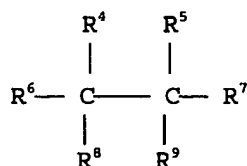
Table 2

	Experimental	Theoretical
F:C ratio	1.86	2.17
%CF <sub>2</sub> group	47.9	83.3
%CF <sub>3</sub> group	18.5	16.7

Claims

1. A method of coating a surface with a polymer layer,  
 5 which method comprises exposing said surface to a pulsed plasma comprising a monomeric saturated organic compound, said compound comprising an optionally substituted alkyl chain of at least 5 carbon atoms optionally interposed with a heteroatom; so as to form an oil or water repellent  
 10 coating on said substrate.
2. A method according to claim 1 wherein the alkyl chains are substituted by halogen.
- 15 3. A method according to claim 2 wherein the alkyl chains are perhalogenated.
4. A method according to claim 1 wherein the monomeric organic compound is a compound of formula (I)

20



25

- where  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$  and  $\text{R}^8$  are independently selected from hydrogen, halogen, alkyl, haloalkyl or aryl optionally  
 30 substituted by halo; and  $\text{R}^9$  is a group  $\text{X}-\text{R}^{10}$  where  $\text{R}^{10}$  is an alkyl or haloalkyl group and  $\text{X}$  is a bond; a group of formula  $-\text{C}(\text{O})\text{O}(\text{CH}_2)_x\text{Y}-$  where  $x$  is an integer of from 1 to 10 and  $\text{Y}$  is a bond or a sulphonamide group; or a group  $-(\text{O})_p\text{R}^{11}(\text{O})_s(\text{CH}_2)_t-$  where  $\text{R}^{11}$  is aryl optionally substituted by



halo, p is 0 or 1, s is 0 or 1 and t is 0 or an integer of from 1 to 10, provided that where s is 1, t is other than 0.

5 5. A method according to claim 4 wherein the compound of formula (I) comprises a C<sub>6-25</sub>alkane optionally substituted by halogen.

6. A method according to claim 5 wherein the C<sub>6-25</sub> alkane is a C<sub>6-25</sub> perfluoroalkane.

10

7. A method according to any one of the preceding claims wherein the substrate is a fabric, metal, glass, ceramics, paper or polymer material.

15 8. A method according to claim 7 wherein the substrate is a cellulosic fabric.

9. A method according to claim 7 wherein the substrate is a synthetic fabric.

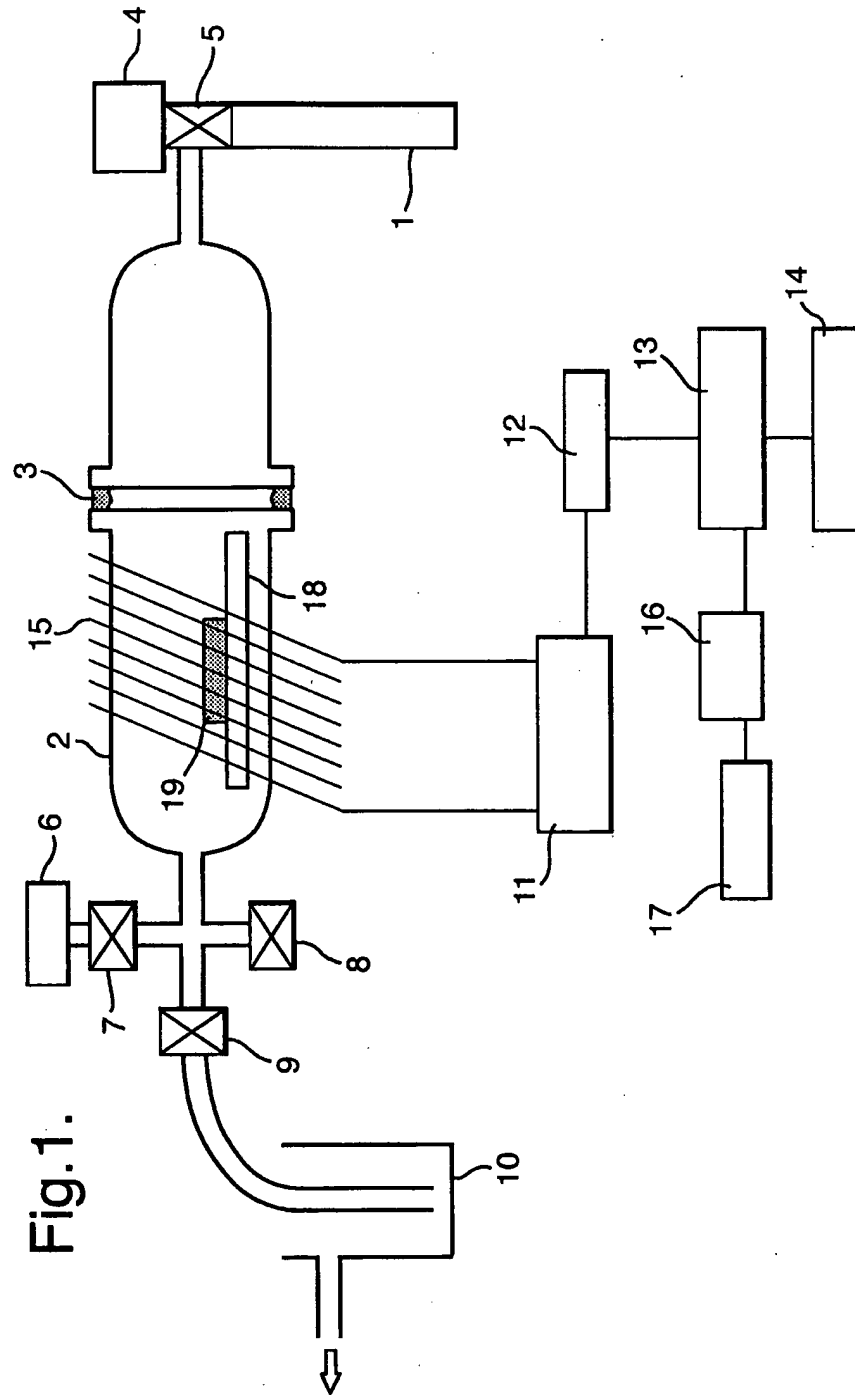
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10. A method according to any one of the preceding claims wherein the monomeric organic compound is in the form of a vapour at a pressure of from 0.01 to 10 mbar.

25 11. A method according to any one of the preceding claims wherein the plasma is created by applying an alternating frequency voltage.

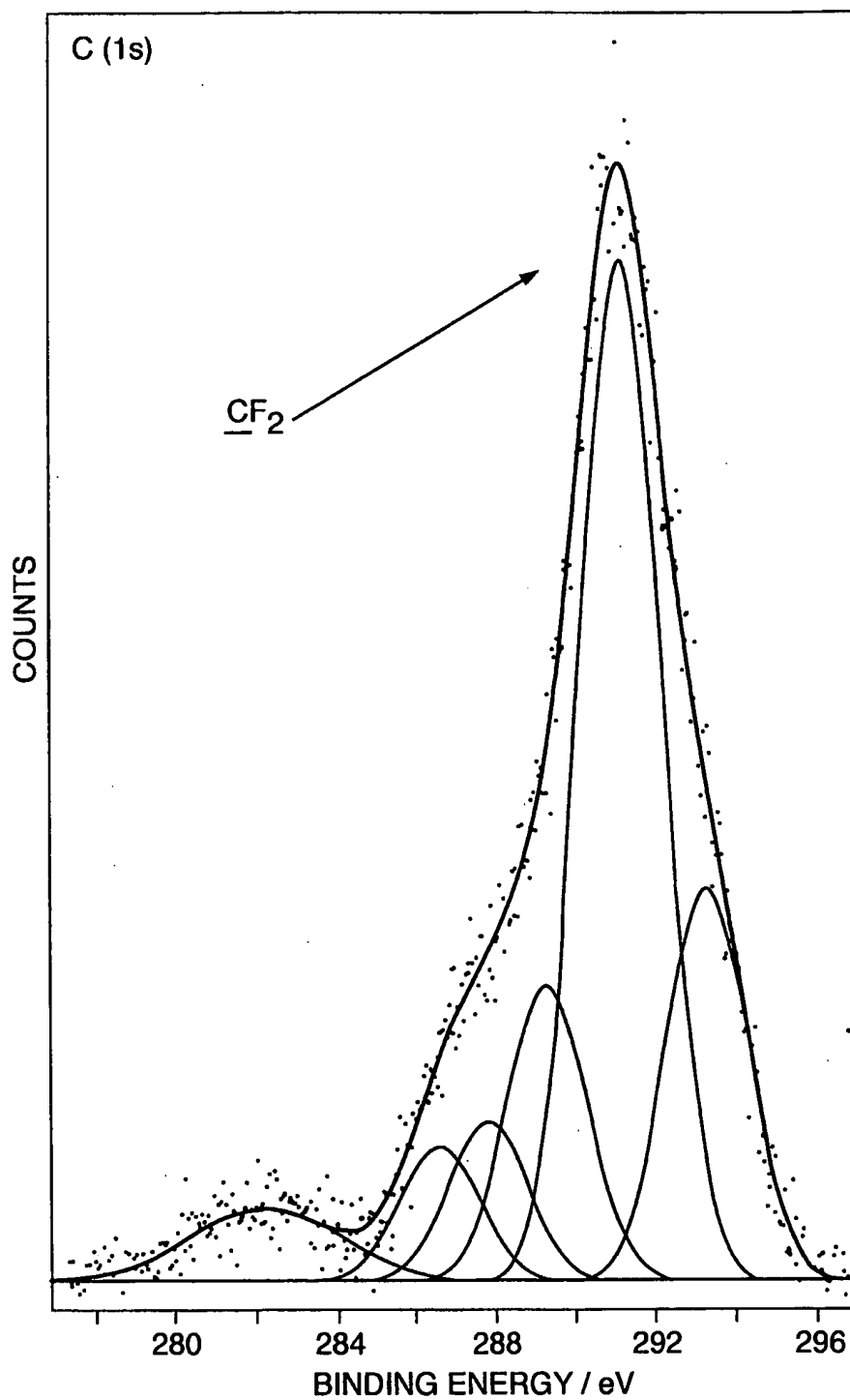
30 12. A method according to any one of the preceding claims wherein the average power of the electrical field applied is up to 50W.

13. A method according to any one of the preceding claims wherein the pulsed fields are applied in a sequence which yields an average power of less than 10W.
- 5 14. A method according to claim 13 wherein the average power is less than 1W.
15. A method according to claim 13 or claim 14 wherein the pulses are applied in a sequence in the power is on for  
10 20 $\mu$ s and off for from 10000 $\mu$ s to 20000 $\mu$ s.
16. A method according to any one of the preceding claims wherein the pulses are applied at a variable rate.
- 15 17. A method according to claim 16 wherein the length of the pulses decreases during the treatment.
18. A hydrophobic or oleophobic substrate which comprises a substrate comprising a coating of an alkyl polymer  
20 obtained by a method according to any one of the preceding claims.
19. The use of an optionally substituted alkane or optionally substituted cycloalkane having at least 5 carbon  
25 atoms in the production of water and/or oil repellent coatings by pulsed plasma deposition methods.
20. The use of claim 19 wherein the alkane or cycloalkane is perhalogenated.
- 30 21. A method for producing an water and/or oil repellent coating on a substrate, substantially as hereinbefore described with reference to the Example.



2/2

Fig.2.



## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 99/02121

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B05D7/24 C23C16/50 D06M10/10 D06M10/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B05D C23C D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 99 32235 A (BTG INT LTD ;BADYAL JAS PAL SINGH (GB); HUTTON SIMON JAMES (GB)) 1 July 1999 (1999-07-01) page 10; claims ---	1-7, 10-13, 18-21
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Y	the whole document ---	8, 9
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## INTERNATIONAL SEARCH REPORT

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